

# **Ion Beam Deposited Cu-Mo Coatings as High Temperature Solid Lubricants**

K.J. Wahl<sup>1</sup>, L.E. Seitzman, R.N. Bolster, and I.L. Singer

*U.S. Naval Research Laboratory, Washington, DC 20375-5342*

M.B. Peterson

*Wear Sciences Corp., Arnold, MD 21012*

Received 26 August 1995; accepted 25 January 1996

---

## **Abstract**

Thin coatings of Cu-Mo were deposited on alumina substrates via ion-beam deposition (IBD). Structure and composition of the coatings were examined using X-ray diffraction, X-ray photoelectron spectroscopy, and micro-Raman spectroscopy. Sliding tests of coated and uncoated substrates were performed in air under reciprocating sliding conditions against alumina ball counterfaces; mean Hertzian contact pressures were 1.0 and 1.6 GPa and test temperatures were between 25°C and 650°C. The as-deposited coatings were metallic and amorphous, but after exposure to temperatures  $\geq 530^\circ\text{C}$ , they converted to oxides containing  $\text{CuMoO}_4$  and  $\text{MoO}_3$ . With increasing temperature, the friction coefficients of the IBD Cu-Mo coatings decreased from  $\sim 0.5$  to  $\sim 0.2$ . At high temperature, the coatings were capable of sustaining low friction sliding ( $\mu \sim 0.2$ ) for 3000 cycles. At high load and temperature, the ball wear coefficient against the IBD Cu-Mo coated alumina was 20 to 100 times less than that of uncoated alumina. The low friction observed at high temperatures was attributed to transformation of the coatings to crystalline oxides, which are known to be lubricious at elevated temperatures.

**Keywords:** friction; wear; solid lubrication; ion-beam deposition

---

## **1. Introduction**

Metal components and traditional lubricants cannot withstand the high temperatures reached by machines like advanced low heat rejection engines. Ceramics could be used as replacement materials because of their good high temperature properties (thermal stability, low thermal conductivity, light weight,...). However, their friction and wear properties are too poor to sustain sliding [1,2], and some form of lubrication must be supplied. Oxide and double oxide (notably molybdates, tungstates, and rhenates [3,4,5,6]) powders have been investigated as high temperature lubricants because of their chemical stability at high temperatures. Unfortunately, metal oxide powders are difficult to attach to surfaces. On the other hand, metals and oxides are readily applied to surfaces by energetic deposition techniques including pulsed laser deposition [7], ion-beam deposition [8], and ion-beam mixing [9].

In this paper, we investigate the friction and wear of alumina sliding against alumina coated with a Cu-Mo alloy deposited by ion-beam deposition (IBD). The purpose of the investigation was to examine whether IBD metal coatings can produce adherent, lubricating oxide films at high temperatures. The Cu-Mo system was chosen because previous investigations have shown that  $\text{CuMoO}_4$  powders, as well as mixtures of  $\text{CuO}$  and  $\text{MoO}_3$  powders, are effective solid lubricants at high temperatures; these oxides can provide friction coefficients of 0.2-0.3 at temperatures  $>600^\circ\text{C}$  [3]. Here we report on recip-

rocating sliding tests of IBD Cu-Mo coatings conducted at temperatures from 25-650°C. Analytical studies and thermochemistry are used to relate the friction behavior to oxidation and phase changes in the coating that occur during heating and sliding in air.

## **2. Experimental**

Dual ion-beam deposition (IBD) was used to deposit Cu-Mo coatings on alumina substrates. The deposition chamber was equipped with 3 Kaufman type ion sources; one ion gun was used to sputter clean the substrate before deposition, while the other two ion guns were used to deposit Cu and Mo from targets [10,11]. The two target IBD system provides the ability to control compositions of binary (and ternary) alloys over wide ranges. Coatings were deposited at room temperature onto polycrystalline  $\alpha$ -alumina substrates (2.5 cm diameter) polished to a rough surface finish (last step 15 mm diamond). Two deposition runs with three substrates arranged along a line were performed; based on earlier deposition studies [10,11], coating composition was expected to vary by  $\pm 10$  at.% over the sample deposition region. Coating thickness was measured on a glass witness coupon using interference microscopy.

Coating structure was investigated using X-ray diffraction (XRD) performed in the standard  $\theta/2\theta$  configuration using a rotating Cu anode, operated at 50 kV and 200 mA. Coating chemistry was examined by Raman analysis,

| Report Documentation Page  |                                    |                                     | Form Approved<br>OMB No. 0704-0188       |   |                                 |
|--|------------------------------------|-------------------------------------|--|---|---------------------------------|
| Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. |                                    |                                     |  |   |                                 |
| 1. REPORT DATE<br><b>1997</b>  |                                    | 2. REPORT TYPE                      |  | 3. DATES COVERED<br><b>00-00-1997 to 00-00-1997</b> |                                 |
| 4. TITLE AND SUBTITLE<br><b>Ion Beam Deposited Cu-Mo Coatings as High Temperature Solid Lubricants</b>   |                                    |                                     | 5a. CONTRACT NUMBER                      |   |                                 |
|  |                                    |                                     | 5b. GRANT NUMBER                         |   |                                 |
|  |                                    |                                     | 5c. PROGRAM ELEMENT NUMBER               |   |                                 |
| 6. AUTHOR(S)   |                                    |                                     | 5d. PROJECT NUMBER                       |   |                                 |
|  |                                    |                                     | 5e. TASK NUMBER                          |   |                                 |
|  |                                    |                                     | 5f. WORK UNIT NUMBER                     |   |                                 |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br><b>Naval Research Laboratory, Center for High Assurance Computer Systems, 4555 Overlook Avenue, SW, Washington, DC, 20375</b>  |                                    |                                     | 8. PERFORMING ORGANIZATION REPORT NUMBER |   |                                 |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  |                                    |                                     | 10. SPONSOR/MONITOR'S ACRONYM(S)         |   |                                 |
|  |                                    |                                     | 11. SPONSOR/MONITOR'S REPORT NUMBER(S)   |   |                                 |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT<br><b>Approved for public release; distribution unlimited</b>  |                                    |                                     |  |   |                                 |
| 13. SUPPLEMENTARY NOTES  |                                    |                                     |  |   |                                 |
| 14. ABSTRACT   |                                    |                                     |  |   |                                 |
| 15. SUBJECT TERMS  |                                    |                                     |  |   |                                 |
| 16. SECURITY CLASSIFICATION OF:  |                                    |                                     | 17. LIMITATION OF ABSTRACT               | 18. NUMBER OF PAGES<br><b>7</b>                     | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT<br><b>unclassified</b>   | b. ABSTRACT<br><b>unclassified</b> | c. THIS PAGE<br><b>unclassified</b> |  |   |                                 |

X-ray photoelectron spectroscopy (XPS) and sputter depth profiling. Raman spectra were acquired with a Renishaw micro-Raman system (2 mm spatial resolution) equipped with a HeNe laser. XPS was performed with monochromated Al X-rays using a Surface Science Instrument (SSI) small-spot analyzer. Sputter depth profiling was accomplished using a 3 keV Ar<sup>+</sup> ion beam which bombarded the sample 50° from the sample normal. Composition profiles were calculated using the SSI data analysis software with Scofield cross sections. These compositions should be considered approximate, however, since preferential sputtering is likely to occur in this system (see e.g. [12]).

Friction and wear tests were performed using ball vs. flat geometry under reciprocating sliding conditions in air at constant temperatures from 25°C to 650°C. Balls were 1.27 cm diameter polycrystalline  $\alpha$ -alumina and the sliding speed was 1 mm/s. Two different test rigs were used: 1) a low load rig [13], operated at a load of 13 N (mean initial Hertzian pressure  $P_H = 1$  GPa) and 2) a high load rig [14] at a load of 58 N (mean initial  $P_H = 1.6$  GPa). Coatings were brought to the test temperature and held there for approximately one hour during testing. Friction coefficients were recorded by computer at 1 sec intervals on the low load rig and recorded continuously via a chart recorder on the high load rig. For reference, sliding tests were also performed on the high load rig with CuO/MoO<sub>3</sub> powder mixtures (50/50 at.%) as well as bare alumina.

Wear tracks and ball wear scars were examined using optical (Nomarski) microscopy. Ball wear volume,  $V$ , was calculated from wear scar diameters (see for example [15]). Ball wear factors,  $k$ , were calculated using the equation

$$k = \frac{V}{LD} \left( \frac{\text{mm}^3}{\text{Nm}} \right) \quad (1)$$

where  $V$  = wear volume in mm<sup>3</sup>,  $L$  = load in Newtons, and  $D$  = total sliding distance in meters [16]. Wear tracks were examined using XPS sputter depth profiling and micro-Raman spectroscopy.

### 3. Results

#### 3.1. Material characterization

Coating thickness was found to be ~200 nm, and the as-deposited coatings appeared gray. After tests at 300°C, coatings darkened to a blue/purple/yellowish color. After tests between 530°C and 650°C, coatings were yellow. Coatings were adherent both before and after heating.

XPS depth profiles (not shown) indicated that the average composition of the as-deposited coatings was approximately 70% Mo, 30% Cu. However, the near surface region of the coatings were Cu rich, and the concentration of C and O was low throughout. XPS depth profiles of coatings tested at 300, 530 and 650°C are shown in Figure 1. After heating to 300°C, the coating was further enriched in Cu at the surface and depleted in the bulk.

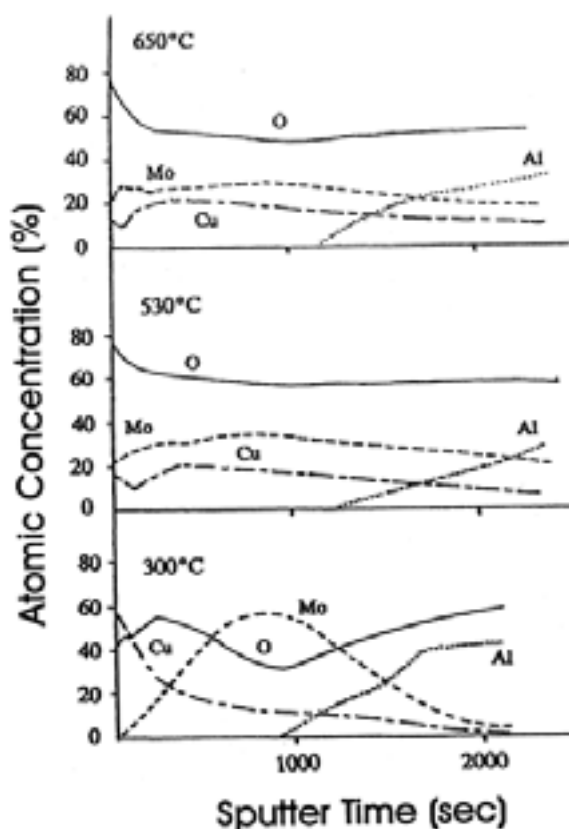


Figure 1. XPS depth profiles of unworn coatings after testing at 300, 530, and 650°C.

Oxygen was present at about 40-60 at.%. At higher temperatures, Mo, Cu, and O were more uniformly distributed throughout the bulk, with no Cu enhancement at the surface. The Mo/Cu ratio was smaller at 650°C than at 530°C. For all the coatings, the profile at the interface between the coating and the alumina substrate was very broad; this is attributed to a sputter shadowing artifact that results from oblique angle sputtering of a roughly polished surface.

XRD spectra of as-deposited coatings and those tested at 300, 530, and 650°C are shown in Figure 2. As-deposited coatings were amorphous. Coatings tested at 300°C still appeared amorphous, although there was an increase in intensity between 20° < 2θ < 30° where CuMoO<sub>4</sub> (copper molybdate) peaks are located. Additionally, the presence of CuO or Cu<sub>2</sub>O cannot be ruled out, due to interference from substrate alumina peaks. Coatings tested at 530 and 650°C had peaks that correspond to the crystalline oxides CuMoO<sub>4</sub> and MoO<sub>3</sub>. It should be noted that the copper molybdate phase identified here may be one of many nonstoichiometric copper molybdates (Cu<sub>x</sub>Mo<sub>y</sub>O<sub>4+z</sub>) [17,18,19]. For simplicity, these phases will be referred to as CuMoO<sub>4</sub>. Coating phases identified by XRD are summarized in Table 1.

XRD spectra of the 50/50 at.% CuO/MoO<sub>3</sub> powder mixtures (before heating, and after heating to 300 and 530°C) were obtained and compared to XRD spectra of CuO, MoO<sub>3</sub>, CuMoO<sub>4</sub> reference powders. Both CuO and MoO<sub>3</sub> phases were present after heating the powder mix-

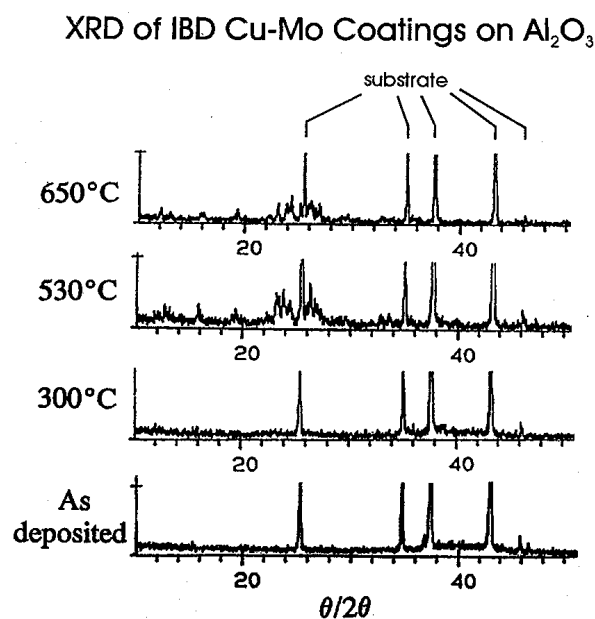


Figure 2. XRD spectra of IBD Cu-Mo coatings, as-deposited and after heating to 300, 530, and 650°C.

tures to 300°C. By 530°C, copper molybdate ( $\text{CuMoO}_4$ ) had formed; some residual  $\text{CuO}$  and  $\text{MoO}_3$  was also detected, perhaps as a result of incomplete mixing. A summary of the phases identified in the powder mixtures is also shown in Table 1.

Micro-Raman spectra were taken on the coatings and oxide reference powders. Spectra of as-deposited and three heated coatings are shown in Figure 3, and the peak identification summarized in Table 2. Spectra obtained from as-deposited coating were featureless. The 300°C coating had a feature at  $\sim 300 \text{ cm}^{-1}$ , consistent with  $\text{CuO}$  [20,21]. The 530°C coating had features indexing to the  $\text{CuMoO}_4$  and  $\text{MoO}_3$  reference powders. Coatings heated to higher temperatures (600, 650°C) had spectra consistent with the  $\text{CuMoO}_4$  reference powders. The broad feature present at  $\sim 500 \text{ cm}^{-1}$  in the 600°C coating has not been identified.

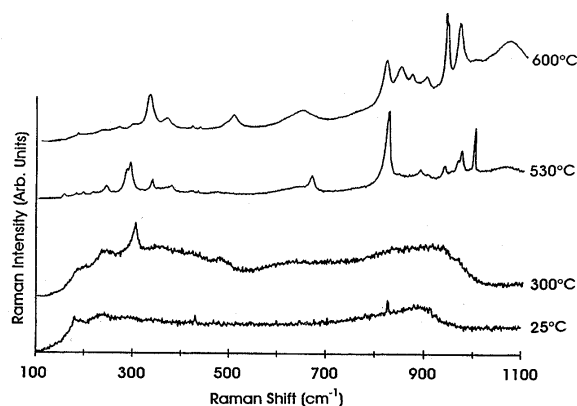


Figure 3. Micro-Raman spectra of unworn IBD Cu-Mo coatings as-deposited and after heating to 25, 300, 530, and 650°C.

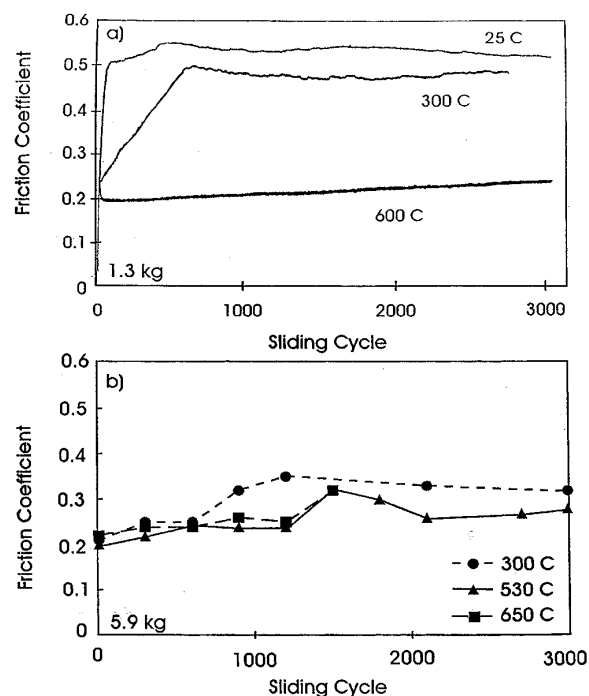


Figure 4. Friction coefficients as a function of sliding cycle and test temperatures for IBD Cu-Mo coatings on alumina. at (a) 13 N and (b) 58 N load.

### 3.2 Tribological behavior

Friction coefficients as a function of cycle are shown in Figure 4a for coatings tested between 25 and 600°C at 13 N load. At 25°C, the friction coefficient rose quickly to  $\sim 0.5$  and remained high for the duration of testing. At 300°C, the friction rise was slower (over the first 700 cycles), then remained between 0.45 and 0.5. A significant reduction in friction coefficient was observed at 600°C; as can be seen from the plot, low friction (0.2) sliding was obtained for over 3000 cycles. Friction data obtained at 58 N, between 300 and 650°C, is shown in Figure 4b. The friction coefficient ranged between 0.2 and 0.35 under these conditions. The test at 650°C was stopped after 1500 cycles due to a malfunction of the rig.

Friction coefficients, averaged between 900 and 3000 sliding cycles for both loads, are plotted as a function of temperature in Figure 5. The average friction coefficient decreased monotonically as the temperature increased from 25 to 650°C. Also plotted in Figure 5 are friction coefficients obtained for the 50/50 at. %  $\text{CuO}/\text{MoO}_3$  powder mixtures. Similar reduction of friction coefficient with increasing temperature was observed for both the powder mixtures and IBD Cu-Mo coatings.

Investigation of the coating wear track by optical microscopy indicated a smoother appearance of tracks at higher temperatures (530–650°C) than at lower temperatures (25, 300°C). Material similar in appearance to the unworn regions remained in the lower regions (valleys). Worn ball surfaces were also examined optically; as in the tracks, the center of the contact zone was smoother at higher tem-

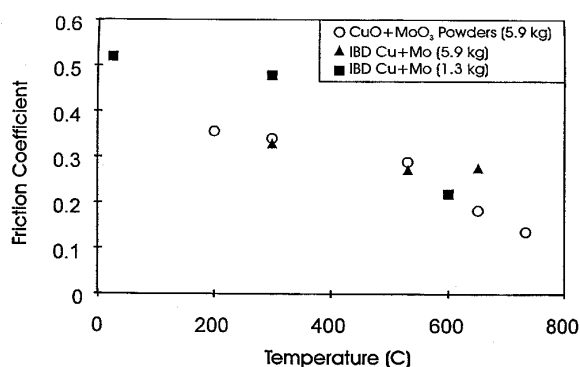


Figure 5. Average friction coefficient vs. testing temperature for both IBD Cu-Mo coatings and 50/50 at.% CuO/MoO<sub>3</sub> powder mixtures.

peratures. Debris around the contact zone had the same color as the corresponding coating, again dependent on testing temperature. The size of the ball wear scar decreased substantially at higher temperatures. Ball wear factors for the various tests against the Cu-Mo coatings and uncoated alumina were calculated using equation (1) and are shown in Figure 6. For tests against the IBD Cu-Mo coatings at 13 N load, the ball wear factor decreased by an order of magnitude when the temperature was increased from 25°C to 300 and 600°C. At the higher load (58 N), ball wear factors obtained after sliding against an uncoated alumina specimen at 380°C were 20 to 100 times greater than for coated specimens tested between 300 and 650°C.

Wear tracks were also examined by both XPS depth profiling and micro-Raman spectroscopy. XPS depth profiles of 300°C and 650°C wear tracks worn at 58 N load showed Mo and Cu as well as alumina. Sputter depth profiling in and out of the tracks indicated that the coatings were thinned substantially during sliding. Micro-Raman analysis of wear track surfaces is summarized in Table 2. The alumina was observed at high spots in all tracks, while spectra consistent with the bulk coatings were obtained in

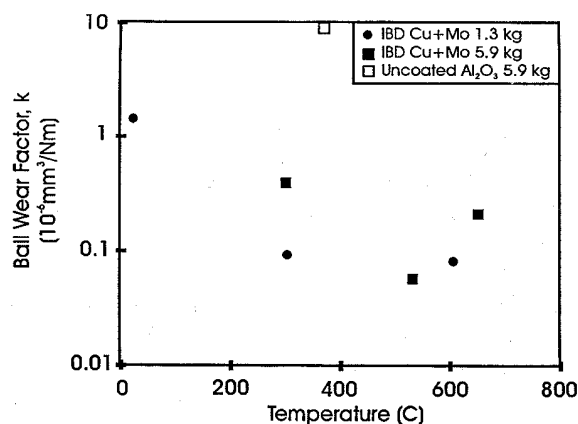


Figure 6. Ball wear factor,  $k$ , for IBD Cu-Mo coated alumina substrates at various loads and temperatures. The ball wear factor for an alumina ball sliding against an uncoated alumina substrate at 380°C is shown for comparison.

the valleys, indicating that the coatings were worn away during sliding. The wear track from the 530°C test contained both CuMoO<sub>4</sub>- and MoO<sub>3</sub>-like features, in agreement with the bulk coating XRD spectra. Tracks worn at higher temperatures (600, 650°C) had features consistent with CuMoO<sub>4</sub> as well as the unidentified broad hump at 500 cm<sup>-1</sup>.

## 4. Discussion

### 4.1. Chemistry of coatings

Thermochemistry plays a role in many of the changes occurring in the IBD Cu-Mo coatings with heating, most notably oxidation and phase changes. The oxidation behavior of the coatings and powders can be analyzed with the ternary diagram calculated for the Cu-Mo-O system at (530-650°C), shown in Figure 7. As the oxygen content of a Cu-Mo mixture increases, one expects first the formation of binary Mo and Cu oxide phases, and then a ternary phase. Since there is an excess of Mo in the IBD Cu-Mo coatings, all the Cu will eventually be in the CuMoO<sub>4</sub> phase with excess Mo oxidized to MoO<sub>3</sub>. This is consistent with our experimental observations. Similarly, in the case of the powder mixtures we began with a composition equivalent to CuMoO<sub>4</sub> (point A), along the CuO-MoO<sub>3</sub> tie-line; after heating the powder mixtures between 530 and 650°C, we observed transformation to CuMoO<sub>4</sub>. This is consistent both with what is predicted in Figure 7, as well as with previous investigations of the CuO-MoO<sub>3</sub> system [18]. In addition to CuMoO<sub>4</sub>, both CuO and MoO<sub>3</sub> remained in the powder mixtures after heating; this may be a result of incomplete mixing of the powders.

Two other composition changes can be accounted for by thermochemical processes. First, the reduced Mo/Cu ratio in the coating heated to 650°C is consistent with sublimation of MoO<sub>3</sub>, which begins at ~600°C [22]. Second, segregation of Cu to the coating surface was observed after heating to 300°C; this phase separation is not unex-

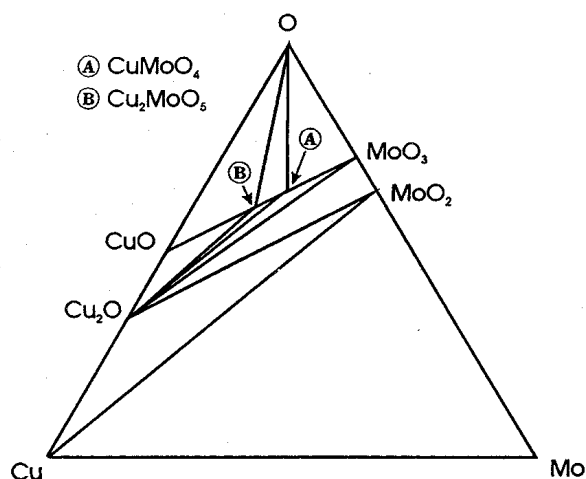


Figure 7. Calculated ternary phases diagram for the Cu-Mo-O system (see accompanying text).



pected since Mo and Cu are immiscible at temperatures below 1083°C [23] (melting point of Cu). Although we cannot explain why Cu segregated to the surface, similar surface segregation has been observed in Cu-Mo thin films heated in air to 300°C [24].

#### 4.2. Coating friction and wear

The coatings in this investigation provided friction coefficients between 0.2 and 0.5. This corresponds to a reduction in friction of 30% to 70% over unlubricated alumina contacts, where friction coefficients are typically 0.7 or higher at similar temperatures [25,26]. Friction coefficients were lowest during tests run at temperatures  $\geq 530^\circ\text{C}$ ; post testing analyses confirmed transformation of the metal coating to the oxide phases  $\text{CuMoO}_4$  and  $\text{MoO}_3$ . The low friction coefficients for the oxidized coatings are comparable to previous data for these oxides tested as powders [4,6]. The friction reducing capabilities of these oxides is believed to be due to the relative softness of the oxide with respect to the substrate [27]. Oxides are known to soften above their ductile-to-brittle transition temperature [28] which is typically  $\sim 0.4 - 0.7 T_m$  [29], where  $T_m$  is the melting point in Kelvin. Therefore,  $\text{CuMoO}_4$  and  $\text{MoO}_3$ , with  $T_m$  values of about  $800^\circ\text{C}$  [17,30], are expected to soften between  $200^\circ\text{C}$  and  $550^\circ\text{C}$ , the temperature range over which the friction coefficient dropped (Fig. 5).

It is well known that unlubricated alumina sliding against itself can result in very high wear rates. Dong et al. [13] have constructed wear maps from wear rates of  $\alpha$ -alumina. These maps indicate "severe" wear at initial contact stresses above  $\sim 1.5$  GPa at temperatures between 200 and  $800^\circ\text{C}$ . We have performed a similar analysis by converting the wear factors shown in Fig. 6 to ball wear rates; we divided our wear factor, given in equation (1), by the Vicker's hardness of alumina ( $H_v$ ) as a function of temperature, using values of  $H_v$  from reference [13]. While the ball wear rate against the uncoated alumina fell into the severe wear regime, the wear rates against the coated substrates were 20 to 100 times smaller and fell in the mild wear regime. Therefore, the coatings were able to reduce counterface wear significantly, despite the high initial contact stress (1.6 GPa).

The reduction in wear of the counterfaces with increasing temperature may be attributed to lower friction coefficients, which results in reduced mechanical stress at the interface. It could also be due to formation of a protective transfer film. Previously Fusaro [31] has shown that soft, ductile films of  $\text{MoS}_2$  on rough surfaces can act as lubricant reservoirs. We speculate that a protective film could be supplied by the softened oxides trapped in the "reservoir valleys" of the roughly polished alumina surface. This "reservoir effect" could account for the 3000 sliding cycles sustained with low friction ( $\mu \sim 0.2$ ) at  $600^\circ\text{C}$ .

We have shown that Cu-Mo alloy coatings can be converted to lubricious oxide coatings by heating in air. We suggest that the ion beam deposition process provided the adhesion needed to keep the coatings on the alumina substrates during oxidation and wear. This approach can easily

be extended to other oxide lubricants [e.g. 5,32], using thermochemical calculations or phase diagrams, where available, to guide the choice of alloys.

## 5. Conclusions

Amorphous IBD Cu-Mo coatings on alumina were shown to behave as solid lubricants at high temperatures, where the friction coefficient fell from 0.5 to 0.2. Friction reduction at elevated temperatures was attributed to the formation of lubricious crystalline oxide phases. The coatings also reduced wear of alumina ball counterfaces by up to two orders of magnitude at high contact stresses.

## Acknowledgements

The authors acknowledge the assistance of L.K. Ives for the tribotesting performed at NIST, C.R. Gossett for RBS analyses, and I.P. Hayward for assistance with the micro-Raman spectroscopy. This work was funded by the ONR tribology program. K.J.W. thanks the National Research Council for support through a NRC/NRL post-doctoral associateship.

## References

- [1] K.H. Habig and M. Woydt, *Proc. of the 5th Intl. Conf. on Trib.*, 3 (1989) 106-113.
- [2] Jahanmir, S. and Dong, X., in S. Jahanmir (ed.) *Friction and Wear of Ceramics*, Marcel Dekker, New York, 1994, pp. 15-49.
- [3] M.B. Peterson, S.F. Murray, and J.J. Florek, *ASLE Trans.*, 2 (1960) 225-234.
- [4] M.B. Peterson, S.J. Calabrese, and B. Stupp, Report No. AD 124248, Defense Tech. Info. Center, Washington, DC 1982.
- [5] M.B. Peterson, S.J. Calabrese, S.Z. Li, and X.X. Jiang, in D. Dowson, C.M. Taylor, M. Godet (eds.), *Mechanics of Coatings*, Leeds-Lyon Symposium 16, Tribology Series 17, Elsevier, Amsterdam, 1990, pp.15-25.
- [6] M.B. Peterson, S.J. Calabrese, S.Z. Li, and X.X. Jiang, *J. Mater. Sci. Technol.*, 10 (1994) 313-320.
- [7] J.S. Zabinski, A.E. Day, M.S. Donley, C. DellaCorte, and N.T. McDevitt, *J. Mater. Sci.*, 29 (1994) 5875-5879.
- [8] F.A. Smidt, *Int. Mater. Rev.*, 35 (1990) 61-128.
- [9] J. Lankford, W. Wei, and R. Kossowsky, *J. Mater. Sci.*, 22 (1987) 2069-2078.
- [10] R.N. Bolster, NRL Report NRL/MR/6176-92-7135 (1992).
- [11] I.L. Singer, R.N. Bolster, L.E. Seitzman, K.J. Wahl, M.B. Peterson, and R.L. Mowery, NRL Report NRL/MR/6176-94-7633 (1994).
- [12] G. Betz and G.K. Wehner, in R. Behrisch (ed.), *Sputtering by Particle Bombardment II*, (Springer-Verlag, Berlin, 1993) pp 11-90.
- [13] X. Dong, S. Jahanmir, and S.M. Hsu, *J. Am. Ceram. Soc.*, 74 (1991) 1036-1044.
- [14] E.F. Finken, S.J. Calabrese, and M.B. Peterson, *Lub. Eng.*, 29 (1973) 197-204.
- [15] E.P. Whitenon and P.J. Blau, *Wear*, 124 (1988) 291-309.
- [16] K. Holmberg and A. Matthews, in D. Dowson (ed.) *Coatings Tribology: Properties, Techniques and Applications in Surface Engineering*, Tribology Series Vol. 28, Elsevier, Amsterdam, 1994 p. 53.
- [17] K. Nassau and S.C. Abrahams, *J. Crystal Growth*, 2 (1968) 136-140.
- [18] K. Nassau and J.W. Shiever, *J. Amer. Ceram. Soc.*, 52 (1969) 36-40.
- [19] L. Katz, A. Kasenally, and L. Kihlberg, *Acta Crystallogr. B*, 27 (1971) 2071-2077.

- [20] J. Chrzanowski and J.C. Irwin, *Solid State Comm.*, 70 (1989) 11-14.
- [21] S. Guha, D. Peebles, and T.J. Wieting, *Phys. Rev. B.*, 43 (1991) 13092-13101.
- [22] O. Kubaschewski and B.E. Hopkins, *Oxidation of Metals and Alloys*, (Butterworths, London, 1962) 226.
- [23] P.R. Subramanian and D.E. Laughlin, in T.B. Massalski (ed.) *Binary Alloy Phase Diagrams*, 2<sup>nd</sup> ed., ASM International, Materials Park, OH, 1990, p. 1435-1438.
- [24] J. Li, J.W. Mayer, and E.G. Colgan, *J. Appl. Phys.*, 70 (1991) 2820-2827.
- [25] P.A. Benoy and C. DellaCorte, *Surface and Coatings Techol.*, 62 (1993) 454-459.
- [26] A. Erdemir, G.R. Fenske, R.A. Erck, and C.C. Cheng, *Lubrication Eng.*, 46 (1988) 23-30.
- [27] F.P. Bowden and D. Tabor, *The Friction and Lubrication of Solids*, Part 1 (Clarendon Press, Oxford, 1950) Chapter V.
- [28] H.E. Sliney, T.P. Jacobson, D. Deadmore, and K. Miyoshi, *Ceram. Eng. Soc. Proc.*, 7 (1986) 1039-1051.
- [29] A.G. Atkins and D. Tabor, *Proc. Royal Soc. A*, 292 (1966) 441-459.
- [30] R.C. Weast, (ed.) *CRC Handbook of Chemistry and Physics*, 58<sup>th</sup> Edition, CRC Press, Palm Beach, FL, 1977, p. D-65.
- [31] R.L. Fusaro, *ASLE Trans.*, 25 (1982) 141-156.
- [32] S.F. Murray and S.J. Calabrese, *Lubrication Eng.* 49 (1993) 955-964.

